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Intramolecular heterocyclization and cyclopalladation of selenoanisole substituted propargyl imines: Synthesis and reactivity of Pd–C bond towards alkynes

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ABSTRACT

The intramolecular cyclization of *o*-$SeMeC_6H_4C{\equiv}CC{-}(CF_3)(=NAr)$ with $[PdCl_2(PhCN)_2]$ to dimeric cyclopalladated benzoselenophene has been developed under mild conditions. The reactivity of the new dimeric cyclopalladated benzoselenophene is examined towards insertion of alkynes into Pd–C bond. The reactivity study is also extended to Pd–C bond of dimeric cyclopalladated benzothiophenes towards insertion of alkynes.

1. Introduction

The transition metals catalysed heterocyclization of alkynes with a nucleophile in close proximity to triple bond is a common method for the preparation of variety of heterocycles [1–3]. The palladium-based catalysts are one of the promising candidates to effect this cyclization reactions. This is mainly because of the facile redox interchange between the two stable Pd(II)/Pd(0) oxidation states, compatible with various functional groups, easy availability, low toxicity and relatively low cost of palladium metal [4–6]. Pyrroles, furans, furanones, pyrazoles, isoxazoles, indoles, indolizidinones, pyrimidines, pyridinones, and quinolines are few of the important heterocycles prepared by palladium catalysed heterocyclization [7–11]. Likewise, among the other heterocycles, chalcogen based-heterocycles, benzothiophenes and benzoselenophenes [12–15] have attracted special attention since their core structures are present in a great number of biologically active compounds and functional molecules; in particular, benzo[*b*]thiophenes and thiophenes are prevalent in several compounds that are of pharmaceutical and material interests [16–20]. Selenium analogues of benzo[*b*]thiophenes though, have received limited attentions in the manufacturing of pharmaceutical drugs, their biological activities are well documented in the literature [21,22]. Substitution at 2 and 3 position of chalcogen containing heterocycles are important building blocks for the preparation of potential drugs. The transition metals (including palladium) as catalysts or promoters in the synthesis of chalcogen (sulphur, selenium, and tellurium) containing heterocycles are however incompatible with functionality or lack regioselectivity [23–28] and therefore, have rarely been employed in such cyclization reactions [29,30]. Our research group has recently reported the simultaneous heterocyclization and selective palladacyclization by the treatment of *o*-$SMeC_6H_4C{\equiv}CC{-}(CF_3)(=NAr)$, with $[PdCl_2(PhCN)_2]$ to stable intermediary cyclopalladated benzothiophene, $[(C_8H_4S\text{-}3\text{-})C(CF_3)(=NAr){-}Pd(\mu\text{-}Cl)]_2$ via intramolecular thiopalladation [31]. The isolation of the corresponding intermediary organopalladium compounds in the presence of potentially coordinating group has provided a new route for the synthesis of annulated benzothiophene based-palladium complexes. Further, we reported the catalytic activity of the new class of palladacycles in C–C bond forming reactions [32]; for derivatization and for anti-cancer activity [32,33]. The fact that the simultaneous heterocyclization and selective palladacyclization take place under mild conditions prompted us to develop new selenoanisole substituted alkynes for

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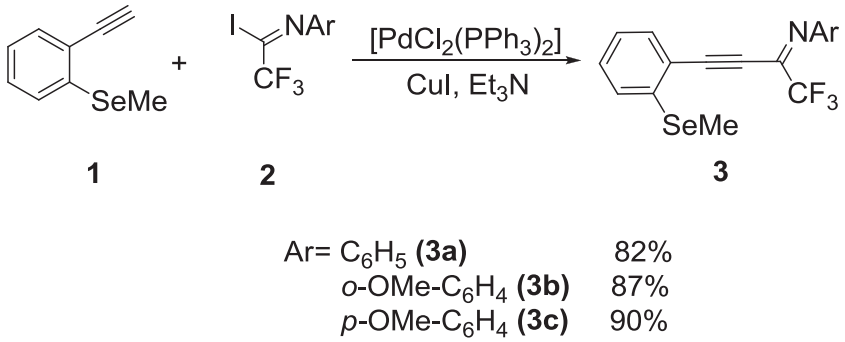


Scheme 1. Synthesis of selenoanisole substituted propargyl imine.

the synthesis of corresponding palladacycles and examine their reactivity through insertion of C≡C into Pd–C bond of palladacycle. The reactivity of Pd–C bond of palladacycles towards alkynes has been well studied by pioneer work of Pfeffer et al. [34–36] and Heck et al. [37,38] However, in this paper, we report the synthesis of cyclopalladated benzoselenophenes derived from selenoanisole substituted propargyl imines (simultaneous formation of heterocycle and metallocycle) and their reactivity with alkynes to benzoseleno[2,3-*c*] pyridinones. The reactivity is also extended with alkynes insertion into Pd–C bond of dimeric cyclopalladated benzothiophenes to benzothieno[2,3-*c*]pyridinones. Pyridinone fused benzothiophenes and benzoselenophenes through insertion of triple bond into Pd–C bond of corresponding cyclopalladated heterocycle lead to formation of new class of multiple fused heterocycles.

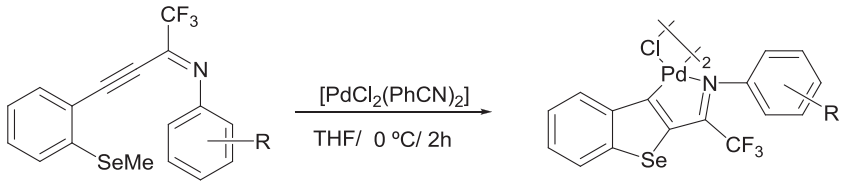
2. Results and discussion

In the modified preparation of *ortho*-selenoanisole substituted perfluoroalkyl propargyl imines (**3**), 2-ethylphenyl methylselane, (**1**) was first prepared in quantitative yield from 2-iodophenyl methylselane [39] and trimethylsillylacetylene (TMSA) using Sonogashira protocol. The reaction of perfluoroalkyl imidoyl iodides, **2** with **1** afforded **3** in good yield in presence of dichorobis(triphenylphosphine)palladium(II) and copper iodide as co-catalyst (Scheme 1). Various *ortho*-selenoanisole perfluoro propargyl imines were prepared in good to moderate yields. All the propargyl imines are characterized by ^{1}H NMR, ^{13}C NMR, and mass spectrometry.

The palladation of *ortho*-selenoanisole perfluoro propargyl imines was proceeded with stoichiometric amount of dichorobis(-triphenylphosphine)palladium(II) in dry THF solvent at 0 °C. The reaction was completed in 2 h and furnished air and moisture stable bright orange solid along with small amount of intact starting material after workup and separation by ether washing. The solid palladacycle, **4c** was isolated in good yield and characterized by ^{1}H NMR, ^{13}C NMR, and IR spectroscopy. The ^{13}C NMR and IR spectra of **3c** showed characteristic resonances of a C≡C bond at 84.77 and 97.92 ppm and a stretching frequency at 2180 cm^{-1}, respectively, which are absent upon the cyclopalladation in **4c**. Similarly, the ^{1}H NMR spectra of **4c** clearly shows the absence of a CH_3 signal from the *o*-$SeCH_3C_6H_4$ group. Further, the change in chemical shift from 131 ppm to 165 ppm in the ^{13}C NMR of the imine carbon atom (C=N) suggests the interaction of nitrogen with the palladium atom. To investigate the scope of present cyclization reaction, various palladacycles were prepared by changing the substitutions at aromatic ring of imine. In the previous report, the reaction of dichorobis(triphenylphosphine)palladium(II) with CF_3 substituted propargyl (phenyl)imine did not proceed to the formation of desired cyclopalladated benzothiophene and surprisingly cyclopalladation occurred only with C_4F_9 substituted propargyl (phenyl)imine [31] while in preparation of palladated benzoselenophene, cyclopalladation with CF_3 substituted propargyl (phenyl) imine took place smoothly with dichorobis(triphenylphosphine) palladium(II) to desired product(**4a**) in 70% yield (Scheme 2). All the palladacycles were isolated in good yields and well characterized by ^{1}H NMR, ^{13}C NMR and IR spectroscopy.

The single crystal of **4c** was obtained on slow evaporation of THF at room temperature. The structure of **4c** was ascertained by means of X-ray diffraction. The crystallographic data of the dimeric compound **4c** suggest that the Pd(II) centre is coordinated in a square-planar fashion by the N1, an imine nitrogen atom, and the C3(sp2) vinyl carbon atom on one side and two bridging Cl atoms on other side. The stereochemistry of the palladacycle **4c** was observed as a transoid dimeric form with the asymmetric unit containing one half-molecule and the other half generated by a crystallographic two-fold axis of symmetry similar to previously observed benzothiophene-based palladacycle (Fig. 1).

The possible reaction pathway for the formation of a benzoseleno-based palladacycle is similar to that of



Scheme 2. Cyclopalladation of selenoanisole substituted propargyl imine.

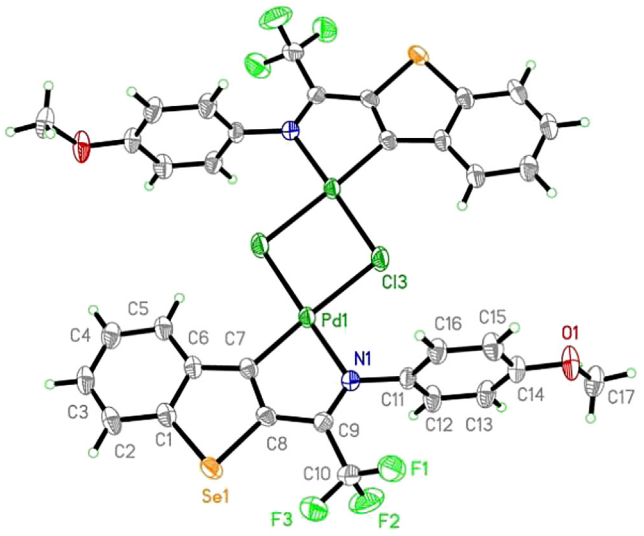


Fig. 1. The molecular structure of **4c**, with the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radius. Unlabelled atoms are generated by the inversion centre (−*x*, −*y*, −*z*).

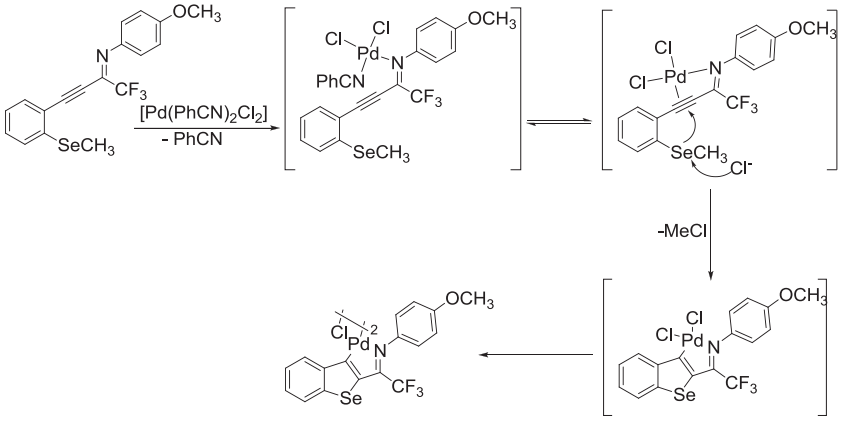
benzothiophene-based palladacycle (Scheme 3) [31]. In the proposed mechanism, we speculate that first step involves the coordination of the N atom followed by interaction of the triple bond to the palladium metal. The triple bond coordinated to a Pd centre undergoes selectively intramolecular seleno addition. In intramolecular nucleophilic addition, the electronically rich seleno group attacks the activated triple bond, followed by the removal of methyl group via S_N2 nucleophilic displacement by the Cl anion present in the reaction medium. The change in chemical shift of neighbouring proton to alkyne in the aromatic ring is shifted from 7.42 to 9.42 ppm. In the benzothio-based palladacycle preparation the chemical shift for this proton was observed at 8.42 ppm, whereas in the present case chemical shift of the proton was observed at 9.42 ppm.

Next, we examined the reactivity of these palladacycles towards alkynes. It has been seen that imine or amine coordinated palladacycles usually undergo insertion of alkyne into Pd–C bond of di-μ-chloro-bridged dimer to form quaternary ammonium halide salts [40]. Taking into consideration the presence of imine nitrogen coordinated to the palladium, we directed our efforts towards the insertion of diphenyl acetylene (DPA) into Pd–C bond. Palladacycles, **4a** was allowed to react with DPA in different solvents, temperatures and conditions. Eventually, we found that palladacycle, **4a** (0.15 mmol) in toluene reacts with excess of DPA under refluxing condition for 12 h affords benzoseleno[2,3-*c*] pyridinone in good yields (Scheme 4).

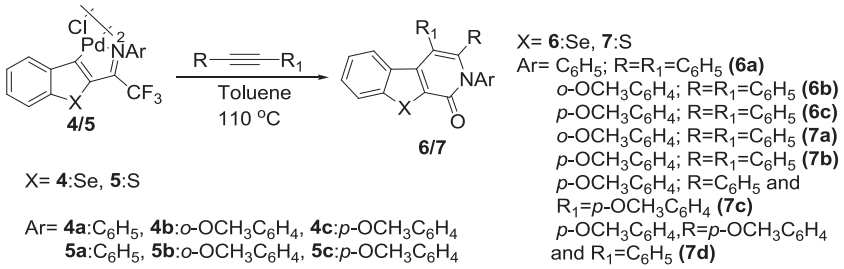
In order to rationale the formation of tricyclic heterocycles **6** and **7**, the proposed mechanism involves generation of seven member ring intermediate after coordination of triple bond to palladium and subsequent insertion into Pd–C bond where palladium interacts with alkynyl carbon followed by heterolytic palladium-carbon cleavage and ring closer. The generation of black palladium metal is evident for the reductive elimination of palladium during the progress of reaction. The formation of benzoseleno[2,3-*c*] pyridinone rather than expected pyridinium salt may be attributed to the presence of CF_3 group bonded to the pyridinium ring carbon. The carbon atom attached to CF_3 is more electrophilic because of highly electronegative nature of CF_3 group which in turn is susceptible to nucleophilic attack by hydroxyl ion and undergoes subsequent oxidation to form carbonyl group (Scheme 5).

The most significant signal in the FT-IR in favour to formation of carbonyl group was evidenced by the appearance of sharp peak at 1645 cm^{-1}(for benzoselenophene pyridinone) and 1653 cm^{-1} (for benzothiophene pyridinone). The chemical shift in ^{13}C NMR [165.2 ppm] for the carbon attached to the CF_3 group of palladacycles was not changed much upon the insertion of C≡C into Pd–C bond [160.0 ppm]. The mass of pyridinone was further confirmed by high resolution mass spectrometry. Finally, the suitable single crystals of **7b** was developed by evaporating the chloroform solvent at 35–40 °C in four days and the structure was ascertained by means of X-ray diffraction study (Fig. 2).

The study on alkyne insertion into Pd–C bond was then extended to the various cyclopalladated benzoselenophenes and benzothiophenes and the corresponding pyridinones were obtained in good yields (Table 1). We have also examined the reactivity of the cyclopalladated benzothiophene towards unsymmetrical acetylene. 1-methoxy-4-(phenylethynyl)benzene reacted smoothly with **4a** to affords mixture of the corresponding isomers, **7c**/**7d** in a 60:40 ratio (the ratio of major to minor regioisomer was calculated using ^1H NMR); these isomers were isolated and characterized without separation of single regioisomer. Thus, the steric and electronic properties of the substituent on the phenyl ring of acetylene do not attract much discrimination in the insertion of unsymmetrical acetylene into the Pd–C bond. While changing the perfluoro group of the benzothiophene based-palladacycle [$-C_4F_9$], we found that under set optimized reaction condition, diphenyl acetylene undergo



Scheme 3. Plausible reaction pathway for the formation of a benzoseleno-based palladacycle.



Scheme 4. Alkynes insertion into Pd–C bond of cyclopalladated benzoselenophene and benzothiophene.

cyclization in presence of palladacycle to afford selectively hexaphenylbenzene and no corresponding pyridinone product was observed (entry 7). In case of mono substituted alkynes, (1-hexyne and phenyl acetylene) the insertion reaction did not proceed to desired cyclized product under set optimized reaction conditions [41–43]. All the products were characterized by ^{1}H NMR, ^{13}C NMR, IR and mass spectrometry.

3. Conclusion

The selective cyclopalladated benzoselenophenes are synthesized from selenoanisole substituted propargyl imine ligands and palladium salt through intramolecular cyclization under mild conditions which otherwise requires coordinating benzoselenophene ligands. The reactivity of the cyclopalladated benzoselenophenes is examined towards alkynes through insertion into Pd–C bond to afford fused heterocycles, benzoseleno[2,3-*c*] pyridinones. The metal-mediated synthesis of benzothieno[2,3-*c*] pyridinones is

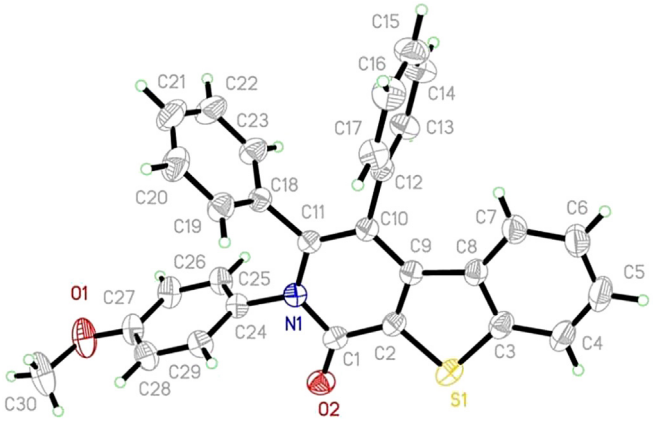
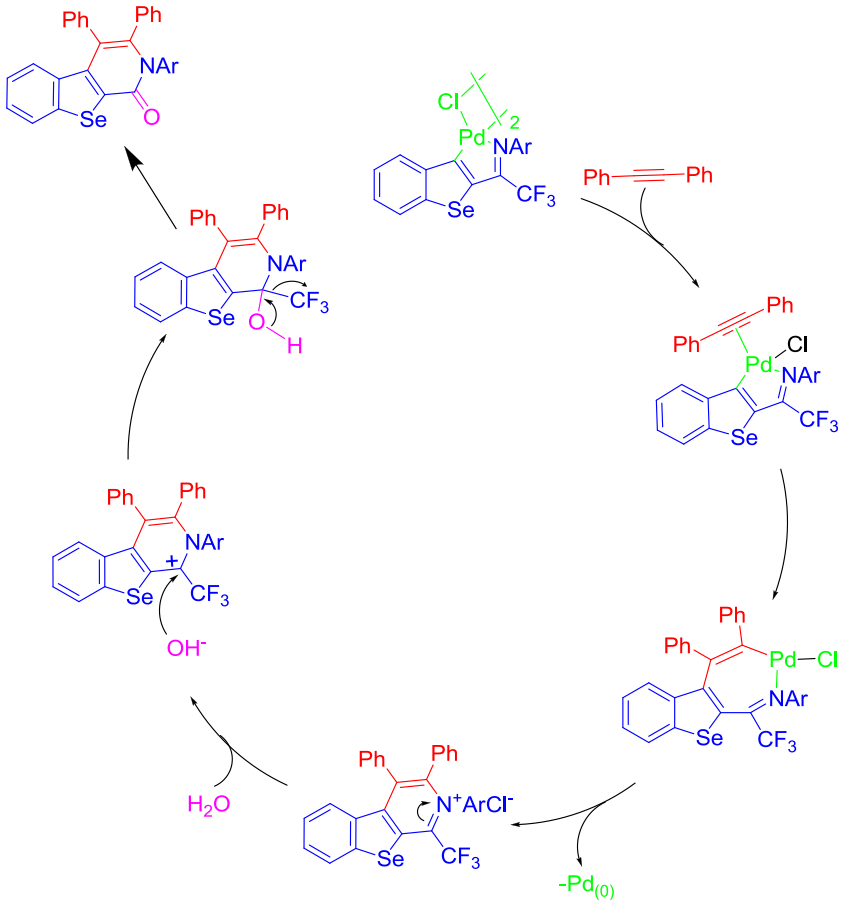


Fig. 2. X-ray structure of benzothieno[2,3-*c*]pyridinone **7b**, with the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radius. Toluene solvate omitted for clarity.



Scheme 5. Plausible reaction pathway for the insertion of alkyne into Pd–C bond of palladacycle.

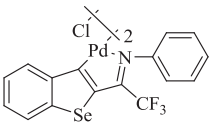
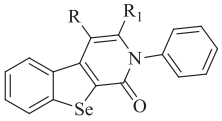
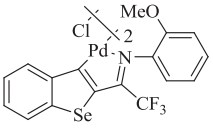
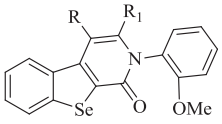
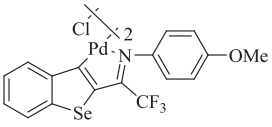
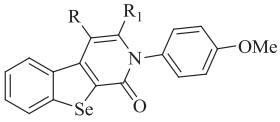
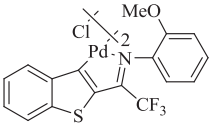
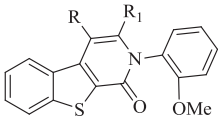
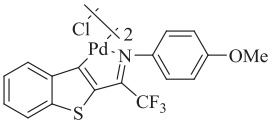
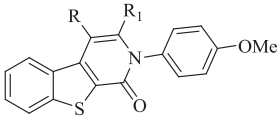
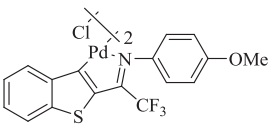
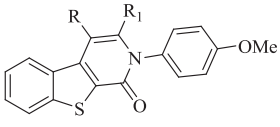
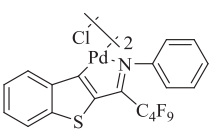
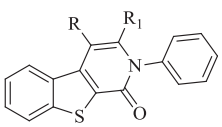
also developed by alkynes insertion into Pd–C bond of cyclopalladated benzothiophene. The reactivity study carried out with the new class of palladacycles reveals that cyclopalladated heterocycles have enormous potential for the synthesis of new class of fused heterocycles through insertion reactions. Investigations towards the catalytic use of palladium salts and photophysical properties of these pyridinones are in progress.

4. Experimental section

4.1. General

All the reactions were carried out in oven dried glassware under an atmosphere of nitrogen. Chemicals were purchased from Aldrich and used as it is unless mentioned otherwise. All the solvents used for reactions were dried before use. Product purification by column chromatography was accomplished using silica gel 60–120 mesh. Technical grade solvents were used for chromatography and distilled prior to use. NMR spectra were recorded in Fourier transform mode. The ^{1}H, ^{13}C and ^{19}F NMR spectra were recorded on a Bruker-Avance (300 MHz), Varian-Inova (400 MHz) and Varian-Inova (500 MHz) spectrometers in $CDCl_3$ and $CFCl_3$ solvents and TMS as the internal standard. Multiplicities in the ^{1}H NMR spectra are described as: s = singlet, d = doublet, t = triplet, q = quartet, qt = quintet, m = multiplet, br = broad; coupling constants are reported in Hz. Infrared spectra were recorded on a Thermo Nicolet Nicolet Nexus 670 spectrometer and reported in cm^{-1}. Low (MS) and high resolution mass spectra (HRMS) were recorded on a Waters 2695 and Thermo Scientific Exactive spectrometer respectively and mass/charge (m/z) ratios are reported as values in atomic mass units. Melting points were recorded on a Toshniwal melting point apparatus.

Table 1
Alkynes insertion into Pd–C bond of cyclopalladated benzoselenophenes and benzothiophenes.

Palladacycles	Product	Yields of isolated product (%)
	 R=R$_1$=Ph:**6a**	61
	 R=R$_1$=Ph:**6b**	67
	 R=R$_1$=Ph:**6c**	71
	 R=R$_1$=Ph:**7a**	69
	 R=R$_1$=Ph:**7b**	78
	 R=*p*-$OCH_3C_6H_4$ and R$_1$=Ph:**7c** R=Ph and R$_1$=*p*-$OCH_3C_6H_4$:**7d**	75
	 R=R$_1$=Ph:**7e**	0

4.2. Typical procedure for the preparation of N-aryl perfluoroalkyl propargyl imines

To a stirred mixture of $[PdCl_2(PPh_3)_2]$ (2 mol%), CuI (4 mol%) in Et_3N (4 mL), alkyne (1 mmol) and *N*-aryl perfluoroalkyl imidoyl iodide (1 mmol) were added successively under N_2 atmosphere. The mixture was stirred at room temperature until the starting materials were consumed. The reaction mixture was filtered and solvent was removed from filtrate under reduced pressure. The crude product obtained was purified by column chromatography using hexane-ethyl acetate mixture(95:5).

4.2.1. Methyl(2-(4-phenyl-3-(trifluoromethyl)but-3-en-1-ynyl) phenyl)selane (**3a**)

Yield: 82% (301 mg), yellow solid, mp 82–84 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.41 (t, $^3J_{HH}$ = 7.7 Hz, 2H), 7.36–7.30 (m, 3H), 7.30–7.23 (m, 3H), 7.14–7.10 (m, 1H), 2.28 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 147.52, 138.36, 134.20, 131.19, 128.93, 128.51, 128.25, 127.41, 125.42, 121.39, 120.59, 116.90, 98.14, 83.93, 6.49 ppm. ^{19}F NMR (376 MHz, $CDCl_3$): δ −71.38 (s, 3F). IR (KBr): 2187, 1265, 1145, 1070, 1040, 800, 759, 693 cm^{-1}. HRMS: Anal. Calcd. for $C_{17}H_{13}NF_3Se$: 368.01598. Found: 368.01692.

4.2.2. (2-(4-(2-Methoxyphenyl)-3-(trifluoromethyl)but-3-en-1-ynyl)phenyl)(methyl)selane (**3b**)

Yield: 87% (346 mg), yellow liquid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.32–7.25 (m, 3H), 7.23–7.14 (m, 2H), 7.13–7.06 (m, 1H), 6.99–6.91 (m, 2H), 3.85 (s, 3H), 2.25 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 149.89, 137.55, 136.53, 133.44, 130.41, 127.54, 127.48, 124.76, 120.17, 119.98, 119.90, 116.34, 111.31, 97.72, 84.04, 56.03, 7.25 ppm. ^{19}F NMR (376 MHz, $CDCl_3$): δ −71.16 (s, 3F). IR (KBr): 2189, 1126, 1144, 1034, 802, 750, 553 cm^{-1}. HRMS: Anal. Calcd. for $C_{18}H_{15}ONF_3Se$: 398.0265. Found: 398.02759.

4.2.3. (2-(4-(4-Methoxyphenyl)-3-(trifluoromethyl)but-3-en-1-ynyl)phenyl)(methyl)selane (**3c**)

Yield: 90% (358 mg), yellow solid, mp 75–77 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.59 (d, $^3J_{HH}$ = 8.8 Hz, 2H), 7.42 (d, $^3J_{HH}$ = 7.5 Hz, 1H), 7.35–7.28 (m, 2H), 7.20–7.11 (m, 1H), 6.91 (d, $^3J_{HH}$ = 8.8 Hz, 2H), 3.85 (s, 3H), 2.34 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 158.80, 139.21, 137.29, 133.37, 130.36, 127.78, 124.93, 124.36, 120.50, 116.81, 113.58, 97.68, 84.70, 55.74, 7.46 ppm. ^{19}F NMR (376 MHz, $CDCl_3$): δ −70.91 (s, 3F). IR (KBr): 2180, 1251, 1119, 1034, 834, 756, 517 cm^{-1}. HRMS: Anal. Calcd. for $C_{18}H_{15}ONF_3Se$: 398.02655. Found: 398.02722.

4.3. Typical procedure for the synthesis of palladacycles

To a solution of $[PdCl_2(PhCN)_2]$ (0.25 mmol) in dry THF (4 mL) at 0 °C, alkyne **3** (0.25 mmol) was added. The mixture was stirred for 2 h at room temperature. The mixture was filtered through celite bed and the filtrate was concentrated to 2 mL. Addition of *n*-hexane (10 mL) to the filtrate afforded orange precipitate. The orange solid was filtered and washed with Et_2O to afford pure palladacycle.

4.3.1. $[(C_8H_4Se\text{-}3\text{-})C(=N\text{–}C_6H_5)(CF_3)Pd(\mu\text{-}Cl)]_2$ (**4a**)

Yield: 70% (87 mg), orange solid. ^{1}H NMR (300 MHz, DMSO-d_6) δ 9.47–9.40 (m, 1H), 7.85–7.79 (m, 1H), 7.74 (s, 1H), 7.36–7.25 (m, 4H), 7.11 (d, $^3J_{HH}$ = 7.4 Hz, 2H). ^{13}C NMR (75 MHz, DMSO-d_6) δ 122.70, 123.34, 124.72, 125.51, 127.07, 127.93, 128.12, 128.60, 129.36, 131.16, 132.09, 132.62, 144.10, 144.50, 145.70, 165.02 ppm. ^{19}F NMR (376 MHz, DMSO-d_6): δ −58.29 (s, 3F). IR (KBr): 1576, 1445, 1332, 1159, 755 cm^{-1}. Elemental analysis: Anal. Calcd. for $C_{32}H_{18}Cl_2F_6N_2Pd_2Se_2$: C, 38.97; H, 1.84; N, 2.84. Found: C, 39.09; H, 1.77; N, 2.97.

4.3.2. $[(C_8H_4Se\text{-}3\text{-})C(=N\text{–}C_6H_4\text{-}o\text{-}OMe)(CF_3)Pd(\mu\text{-}Cl)]_2$ (**4b**)

Yield: 82% (107 mg), orange solid. ^{1}H NMR (300 MHz, DMSO-d_6) δ = 9.47 (d, $^3J_{HH}$ = 7.7 Hz, 1H), 8.11 (d, $^3J_{HH}$ = 7.4 Hz, 1H), 7.48–7.31 (m, 3H), 7.22 (d, $^3J_{HH}$ = 7.6 Hz, 1H), 7.13 (d, $^3J_{HH}$ = 8.1 Hz, 1H), 7.0 (t, $^3J_{HH}$ = 7.6 Hz, 1H), 3.86 (s, 3H). ^{13}C NMR (75 MHz, DMSO-d_6) δ 165.49, 151.84, 145.85, 144.14, 133.3, 132.67, 130.88, 128.59, 128.0, 125.58, 124.77, 124.19, 119.63, 117.32 (q, $^2J_{CF}$ = 283 Hz) 111.41, 55.84. ^{19}F NMR (376 MHz, DMSO-d_6): δ −60.62 (s, 3F). IR (KBr): 1561, 1445, 1160, 753 cm^{-1}. Elemental analysis: Anal. Calcd. for $C_{34}H_{22}Cl_2F_6N_2O_2Pd_2Se_2$: C, 39.03; H, 2.12; N, 2.68. Found: C, 39.12; H, 2.05; N, 2.73.

4.3.3. $[(C_8H_4Se\text{-}3\text{-})C(=N\text{–}C_6H_4\text{-}p\text{-}OMe)(CF_3)Pd(\mu\text{-}Cl)]_2$ (**4c**)

Yield: 85% (111 mg), orange solid. ^{1}H NMR (300 MHz, DMSO-d_6) δ 9.50–9.41 (m, 1H), 7.94–7.84 (m, 1H), 7.40–7.31 (m, 2H), 7.16–7.07 (m, 2H), 6.95–6.85 (m, 2H), 3.82 (s, 3H). ^{13}C NMR (75 MHz, DMSO-d_6) δ 55.31, 113.22, 119.05, 124.67, 125.47, 127.84, 131.09, 132.57, 137.45, 144.0, 145.74, 158.16, 165.20 ppm. ^{19}F NMR (376 MHz, DMSO-d_6): δ −58.22 (s, 3F). IR (KBr): 1552, 1501, 1444, 1251, 1153, 838 cm^{-1}. Elemental analysis: Anal. Calcd. for $C_{34}H_{22}Cl_2F_6N_2O_2Pd_2Se_2$: C, 39.03; H, 2.12; N, 2.68. Found: C, 38.95; H, 2.17; N, 2.59.

4.4. Typical procedure for the synthesis of pyridinone

A mixture of the palladacycle **4**/**5** (0.15 mmol) and diaryl alkyne (1.5 mmol) was refluxed in toluene (15 mL) for 12 h. The resulting mixture was cooled to room temperature and solvent was evaporated under reduced pressure. The residue obtained was dissolved in DCM (25 mL). The palladium black formed was removed by filtration and the filtrate was concentrated and subjected to column chromatography using neutral alumina and DCM/hexane (50/50) to yield solid product **6**/**7**.

4.4.1. 2,3,4-Triphenylbenzo[4,5]selenopheno[2,3-c]pyridin-1(2H)-one (**6a**)

Brown solid (87 mg, 61%) mp 282–284 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.96 (d, $^3J_{HH}$ = 7.9 Hz, 1H), 7.34 (dt, $^3J_{HH}$ = 7.02, $^4J_{HH}$ = 1.1 Hz, 1H), 7.26–7.22 (m, 4H), 7.22–7.19 (m, 3H), 7.17–7.13 (m, 3H), 7.03 (dt, $^3J_{HH}$ = 7.3, $^4J_{HH}$ = 1.1 Hz, 1H), 6.92–6.89 (m, 5H), 6.63 (d, $^3J_{HH}$ = 8.2 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 159.84, 144.04, 143.93, 143.17, 138.84, 138.64, 136.64, 134.10, 132.58, 131.30, 130.95, 129.22, 128.62, 128.31, 127.85, 127.49, 127.34, 127.21, 127.04, 126.36, 124.35, 119.37 ppm. IR (KBr): 1644, 1563, 1477, 1446 cm^{-1}. HRMS: Anal. Calcd. for $C_{29}H_{20}ONSe$: 478.07046. Found: 478.06765.

4.4.2. 2-(2-Methoxyphenyl)-3,4-diphenylbenzo[4,5]selenopheno [2,3-c]pyridin-1(2H)-one (**6b**)

Brown solid (102 mg, 67%) mp 196–198 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.95 (d, $^3J_{HH}$ = 7.9 Hz, 1H), 7.32 (t, $^3J_{HH}$ = 7.9 Hz, 1H), 7.25–7.18 (m, 5H), 7.15 (t, $^3J_{HH}$ = 7.8 Hz, 1H), 7.11 (d, $^3J_{HH}$ = 7.5, 1H), 7.05–6.98 (m, 2H), 6.94–6.86 (m, 4H), 6.82 (t, $^3J_{HH}$ = 7.3 Hz, 1H), 6.74 (d, $^3J_{HH}$ = 8.2 Hz, 1H), 6.64 (d, $^3J_{HH}$ = 8.4 Hz, 1H), 3.75 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 159.50, 154.44, 144.66, 143.87, 143.28, 138.76, 136.83, 134.09, 131.38, 131.34, 130.86, 130.32, 129.77, 129.52, 128.22, 127.81, 127.47, 127.35, 127.05, 126.66, 126.30, 124.23, 120.29, 119.03, 111.37, 55.38 ppm. IR (KBr): 1645, 1500 cm^{-1}. HRMS: Anal. Calcd. for $C_{30}H_{22}O_2NSe$: 508.08103 and observed 508.07831.

4.4.3. 2-(4-Methoxyphenyl)-3,4-diphenylbenzo[4,5]selenopheno [2,3-c]pyridin-1(2H)-one (**6c**)

White solid (108 mg, 71%) mp 314–316 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.95 (d, $^3J_{HH}$ = 7.9 Hz, 1H), 7.33 (t, $^3J_{HH}$ = 7.5 Hz, 1H), 7.25–7.22 (m, 3H), 7.21–7.16 (m, 2H), 7.07–6.99 (m, 3H), 6.97–6.85 (m, 6H), 6.73 (d, $^3J_{HH}$ = 8.7 Hz, 2H), 6.61 (d, $^3J_{HH}$ = 8.4 Hz, 1H), 3.71 (s,

3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 55.34, 113.94, 119.43, 124.33, 126.37, 127.12, 127.21, 127.34, 127.47, 127.86, 128.30, 130.16, 130.94, 131.35, 131.58, 132.52, 134.26, 136.73, 138.66, 143.20, 144.01, 144.48, 158.68, 160.15 ppm. IR (KBr): 1645, 1508, 1249 cm^{-1}. HRMS: Anal. Calcd. for $C_{30}H_{22}O_2NSe$: 508.08103. Found: 508.08099.

4.4.4. 2-(2-Methoxyphenyl)-3,4-diphenylbenzo[4,5]thieno[2,3-c] pyridin-1(2H)-one (**7a**)

Brown solid (95 mg, 69%) mp 264–266 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.93 (d, $^3J_{HH}$ = 8.2 Hz, 1H), 7.41 (t, $^3J_{HH}$ = 7.1 Hz, 1H), 7.27–7.24 (m, 5H), 7.23–7.20 (m, 1H), 7.16 (dt, $^3J_{HH}$ = 6.7, $^4J_{HH}$ = 1.7 Hz, 1H), 7.10 (dd, $^3J_{HH}$ = 7.8, $^4J_{HH}$ = 1.7 Hz, 1H), 7.06 (dt, $^3J_{HH}$ = 6.1, $^4J_{HH}$ = 1.1 Hz, 1H), 7.02–6.99 (m, 1H), 6.94–6.88 (m, 3H), 6.82 (dt, $^3J_{HH}$ = 7.6, $^4J_{HH}$ = 1.1 Hz, 1H), 6.74 (dd, $^3J_{HH}$ = 8.4, $^4J_{HH}$ = 1.0 Hz, 1H), 6.65 (d, $^3J_{HH}$ = 8.4 Hz, 1H), 3.74 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 55.40, 111.43, 117.83, 120.33, 123.21, 124.08, 125.84, 126.71, 127.12, 127.41, 127.53, 127.86, 128.22, 129.67, 129.78, 130.46, 130.96, 131.27, 131.32, 134.04, 135.93, 136.68, 140.34, 142.96, 143.89, 154.58, 158.51 ppm. IR (KBr): 1653, 1500 cm^{-1}. HRMS: Anal. Calcd. for $C_{30}H_{22}O_2NS$: 460.13658. Found 460.13477.

4.4.5. 2-(4-Methoxyphenyl)-3,4-diphenylbenzo[4,5]thieno[2,3-c] pyridin-1(2H)-one (**7b**)

White solid (107 mg, 78%) mp 302–304 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.93 (d, $^3J_{HH}$ = 7.9 Hz, 1H), 7.41 (t, $^3J_{HH}$ = 8.1 Hz, 1H), 7.29–7.18 (m, 3H), 7.10–7.02 (m, 4H), 6.97–6.88 (m, 6H), 6.74 (d, $^3J_{HH}$ = 8.9 Hz, 2H), 6.63 (d, $^3J_{HH}$ = 8.3, 1H), 3.72 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 55.29,113.89, 118.14, 123.23, 124.14, 125.82, 127.12, 127.23, 127.34, 127.48, 128.27, 129.96, 130.21, 130.97, 131.20, 131.49, 134.12, 135.75, 136.50, 140.15, 142.94, 143.62, 158.62, 159.12 ppm. IR (KBr): 1653, 1506, 1248 cm^{-1}. HRMS: Anal. Calcd. for $C_{30}H_{22}O_2NS$: 460.13658. Found: 460.13258.

4.4.6. 2,3-Bis(4-methoxyphenyl)-4-phenylbenzo[4,5]thieno[2,3-c] pyridin-1(2H)-one and 2,4-bis(4-methoxyphenyl)-3-phenylbenzo [4,5]thieno[2,3-c]pyridin-1(2H)-one (**7c** + **7d**)

Brown solid (110 mg, 75%) mp 290–292 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.95–7.89 (m, 1H), 7.46–7.37 (m, 1H), 7.31–7.25 (m, 3H), 7.24–7.15 (m, 2H), 7.14–7.01 (m, 4H), 6.98–6.88 (m, 2H), 6.84–6.70 (m, 5H), 6.60 (d, $^3J_{HH}$ = 8.3 Hz, 1H), 6.46 (d, $^3J_{HH}$ = 8.9 Hz, 1H), 3.80 (s, 1H), 3.74 (s, 2H), 3.72 (s, 1H), 3.62 (s, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 158.23, 143.48, 136.76, 135.80, 134.37, 132.18, 132.13, 131.72, 131.17, 130.91, 130.41, 130.18, 130.12, 128.64, 128.32, 127.42, 127.27, 127.19, 126.54, 125.93, 125.85, 124.18, 124.13, 123.23, 118.43, 113.92, 113.86, 113.66, 112.55, 93.44, 55.27, 55.10, 54.87, ppm. IR (KBr): 1651, 1510, 1247 cm^{-1}. HRMS: Anal. Calcd. for $C_{31}H_{24}O_3NS$: 490.14714. Found: 490.14442.

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